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Radiocarbon dating of bulk peat samples from raised bogs: non-existence of a previously reported 'reservoir effect'?

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Abstract

In 1995, an unexpected reservoir effect was reported in sequences of bulk ^{14}C dates of raised bog peat. In most peat studies bulk ^{14}C dates are used for obtaining chronologies. Therefore it is important to confirm and quantify such a ^{14}C reservoir effect. Five bulk peat samples from the raised bog Engbertsdijksveen were conventionally ^{14}C dated. The same core had previously been precisely dated by ^{14}C AMS dates of carefully selected above-ground plant remains. The existence of a reservoir effect in bulk peat ^{14}C samples could not be confirmed. Other explanations for the reported reservoir effect are discussed.

1. Introduction

Reliable chronologies are crucial for many Quaternary investigations. Radiocarbon dating of Holocene raised bog peat should be straightforward as this peat consists almost entirely of locally grown plant remains. The ^{14}C content (corrected for isotopic fractionation) of plants growing on raised bogs is in equilibrium with atmospheric values, and therefore no reservoir effect (^{14}C age offset) is expected in above-ground remains of such plants (no influence from ^{14}C-depleted carbon, as is the case for many lake and ocean sediments, e.g. Björck et al., 1998).

Kilian et al. (1995, 2000) obtained a high-resolution sequence of ^{14}C AMS dates of selected plant remains from a peat core. Upon matching this sequence with the ^{14}C calibration curve (^{14}C wiggle-match dating; van Geel and Mook, 1989) it appeared that, when giving priority to placing pure *Sphagnum* samples on the calibration curve, *Sphagnum* samples containing some (2–4%) ericaceous rootlets floated ca. 100–150 ^{14}C 'years' above the calibration curve (too old ^{14}C ages; interpreted as a reservoir effect). These results were not expected; rootlets are generally believed to cause younger ^{14}C ages because they penetrate from higher, younger levels (e.g., Shore et al., 1995). Kilian et al. (1995) then proceeded to see whether other peat cores could also possess unidentified ^{14}C reservoir effects.

Indeed, Kilian et al. (1995) found several published peat cores where sequences of bulk ^{14}C dates followed the shape of the ^{14}C calibration curve, but where the matches improved when a positive ^{14}C age offset was assumed for the peat bulk ^{14}C dates (see Fig. 1A–D). The size of the inferred reservoir effect was constant within cores but it differed between the cores that were from different sites; it ranged from 117 to 237 years. The cores had been deposited under a variety of local humidity conditions (hummock, lawn, hollow). All cores encompassed the period from ca. 750 to 400 cal BC when the ^{14}C calibration curve shows a plateau (approximately constant ^{14}C ages), preceded and followed by phases with rapidly changing ^{14}C ages. Such periods with pronounced shapes (especially plateaux) in the ^{14}C calibration curve offer the best possibilities for identifying reservoir effects in sequences of ^{14}C dates (Kilian et al., 1995).

The reservoir effect reported by Kilian et al. (1995) could alter the chronological interpretation of many bulk ^{14}C dated cores from raised bog deposits. Therefore, in the present study, we aimed to investigate the nature of any reservoir effect in bulk ^{14}C dates in raised bog peat.

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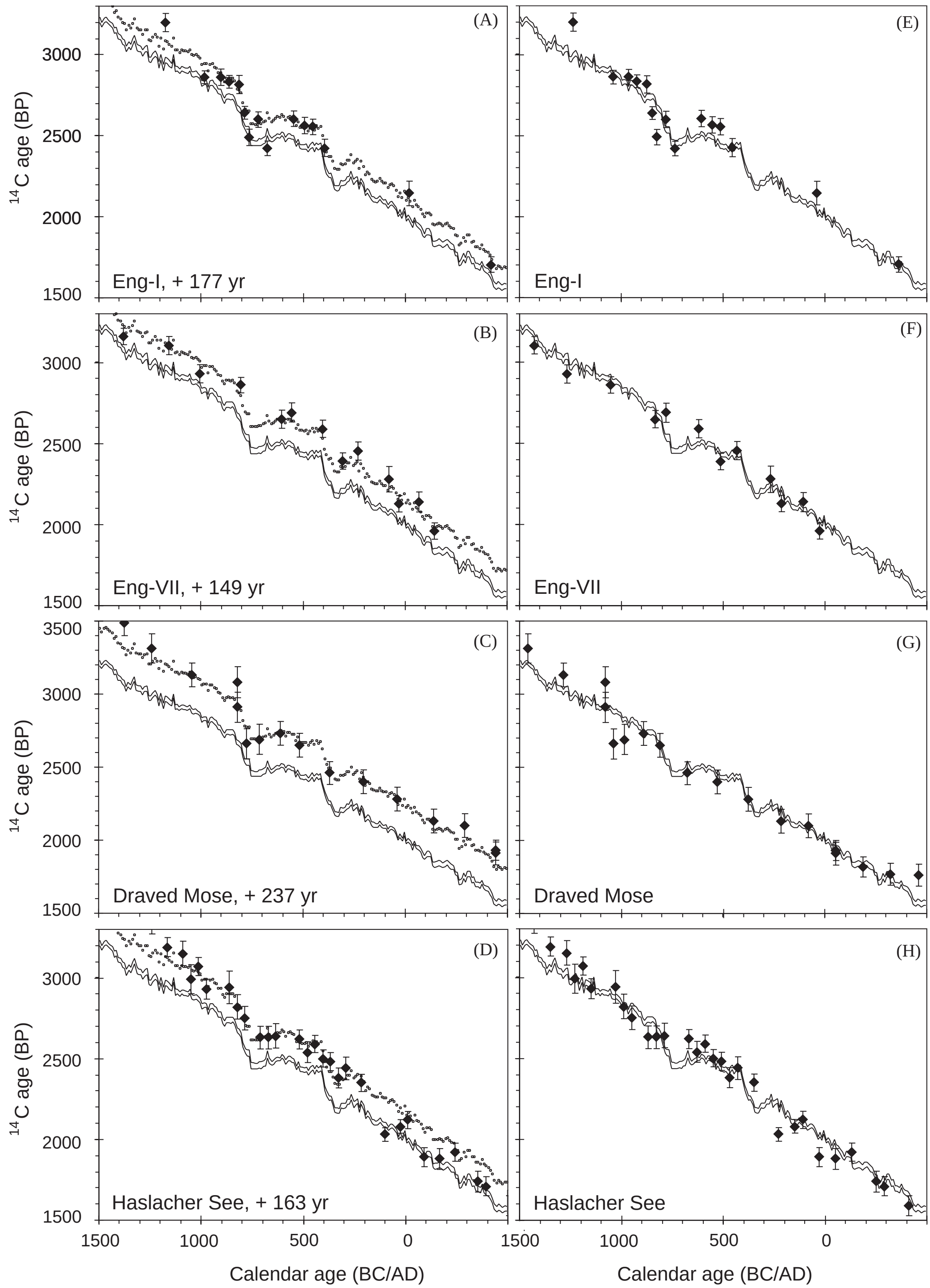

Fig. 1. Four sequences of conventional bulk ^{14}C dates from published peat cores (diamonds with 1 σ error bars) were wiggle-matched against the INTCAL98 ^{14}C calibration curve (lines show 1 σ error envelope; Stuiver et al., 1998). The depicted matches are similar to those proposed by Kilian et al. (1995). A–D show matches when a reservoir effect is assumed. The sizes of the reservoir effects are given after the site names. Small dots indicate where the calibration curve would plot with the chosen reservoir effects. E–H show how each sequence would match without assuming a reservoir effect for the peat bulk dates. Eng-I, The Netherlands: van Geel, 1978; Kilian et al., 1995; Eng-VII (The Netherlands): Dupont and Brenninkmeijer, 1984; Draved Mose (Denmark): Aaby and Tauber, 1975; Haslacher See (Germany): Küster, 1988.

2. Material and methods

Peat core Eng-XV, collected from a raised bog deposit at Engbertsdijksveen in the eastern Netherlands, was ^{14}C wiggle-match dated using a high-resolution sequence of AMS ^{14}C dates of carefully selected and cleaned above-ground plant remains (Blaauw et al., 2003, 2004a). No ^{14}C reservoir effect was assumed. The upper part of the peat core (25 dates) was deposited from ca. 900 to 350 cal BC. As this was a period where the calibration curve shows pronounced fluctuations, a very precise match was obtained (Fig. 2). During the period considered, the core consisted mostly of species that indicate relatively dry local conditions (Table 1).

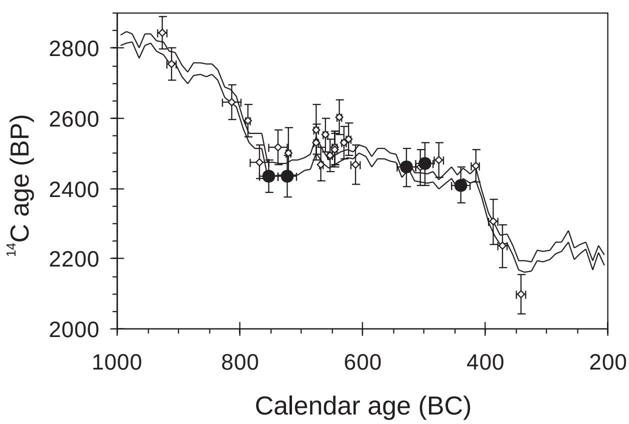

Fig. 2. 25 AMS ^{14}C dates of carefully selected and cleaned above-ground plant remains (open circles; bars indicate 1 σ error limits) from peat core Eng-XV were wiggle-matched to the INTCAL98 calibration curve (lines show 1 σ error envelope; Stuiver et al., 1998; Blaauw et al., 2003). From the same core, 5 bulk peat samples were ^{14}C dated (black circles; bars indicate 1 σ error limits; Table 1).

To confirm the existence of a reservoir effect in ^{14}C dates of bulk peat, five bulk samples were taken from the same core. No roots or rootlets were removed. The samples were AAA treated (Mook and Streurman, 1983) and were ^{14}C dated conventionally (Table 1). The ^{14}C ages were corrected for isotopic fractionation using the δ^{13}C values.

3. Results and discussion

Radiocarbon dates of cleaned above-ground plant remains should reflect ‘true’, contemporaneous ^{14}C ages, because (a) the carbon isotope ratios of above-ground parts of raised bog plant plants are thought to be in balance with atmospheric ^{14}C (some fractionation occurs; see later), (b) ^{14}C ages of sequences of above-ground plant remains could be matched with the ^{14}C calibration curve without assuming a reservoir effect (Fig. 2), and (c) careful selection and cleaning of above-ground macrofossils of different plant species from the same levels did not reveal statistically different ^{14}C ages (see Blaauw, 2003, p. 43).

Several studies cast doubt on the reliability of peat bulk ^{14}C dates (Kilian et al., 1995; Shore et al., 1995; Nilsson et al., 2001). Bulk samples may contain a mixture of material of different ages (above-ground remains, roots, rootlets, fungal mycelium, charcoal, transported fine organic matter, etc.). It therefore is surprising that our conventional bulk peat ^{14}C dates were not significantly different from AMS ^{14}C dates of carefully selected and cleaned above-ground plant

Table 1
Conventional radiocarbon measurements of bulk samples from peat core Eng-XV

Sample	Vegetation composition	C-14 age (BP)	δ^{13}C (‰)	% C	GrN number
57–56 cm	Si (30%) rootl. (60%) Et (10%)	2410 ± 50	−27.61	61.6	27653
61–60 cm	Si (90%) rootl. (5%) Et (5%)	2470 ± 60	−27.33	60.8	27654
63–62 cm	Si (97%) rootl. (3%)	2460 ± 55	−26.31	58.6	27655
76–75 cm	Sa (40%) rootl. (20%) Cv (15%) Et (15%) Ra (10%)	2435 ± 60	−26.93	59.4	27656
78–77 cm	Sa (40%) rootl. (30%) Cv (30%)	2435 ± 45	−27.29	60.9	27657
Pooled KOH extracts	—	2560 ± 55			27872

Cv: *Calluna vulgaris*, Et: *Erica tetralix*, Ra: *Rhynchospora alba*, rootl.: ericaceous rootlets, Sa: *Sphagnum* sect. *Acutifolia*, Si: *S. imbricatum*. Vegetation composition percentages are approximate and are taken from Blaauw (2003) and Blaauw et al. (2004b).

remains from the same levels (Fig. 2). Although the bulk samples with large amounts of ericaceous rootlets tended to give somewhat younger ^{14}C ages than those bulk samples consisting of nearly pure *Sphagnum* (Table 1), the age differences were always smaller than the measurement errors.

The absence of a reservoir effect in the bulk peat samples in the present study needs to be explained. We consider it unlikely that five measurements of samples with different 'true' ^{14}C ages would result in similar ^{14}C age determinations by pure statistical chance. The bulk dates were sampled 4 years after collection of the peat core, while the AMS dates had been taken in the 2 years following collection of the core. Wohlfarth et al. (1998) warn that after prolonged storage, ^{14}C ages can become too young (possibly owing to contamination; however, *Sphagnum*—a major component of raised bog peat—has antimicrobial properties; Painter, 1991). Although this could perhaps point to a removal of an initial reservoir effect, we consider it unlikely that for all bulk samples there was a 'lucky' balance of material giving too old (unidentified reservoir effect sources; Kilian et al., 1995, 2002, but see Pancost et al., 2000), too young (e.g., roots, contamination) and contemporaneous ages, in all cases adding up to similar ages (note that the vegetation composition differed considerably between the samples; Table 1). Moreover, bulk peat samples taken more than a decade after collection of peat core Eng-I (Kilian et al., 1995) gave ^{14}C ages that did not show offsets from ^{14}C dates published earlier (van Geel, 1978; Fig. 1). Perhaps the simplest explanation is that ^{14}C dates of bulk samples of raised bog peat can be accurate after all.

As explained in the introduction, wiggle-matches of sequences of conventional bulk ^{14}C dates from several European raised bog deposits showed a good fit with the calibration curve when a ^{14}C age offset of ca. 100–200 years was assumed for all ^{14}C dates in a sequence (Kilian et al., 1995; Fig. 1A–D). Indeed, when no reservoir effect was assumed, in the studied cores the scatter of the dates became larger and thus the fit became worse (Fig. 1E–H). We discuss two lines of reasoning to assess the supposed reservoir effect reported by Kilian et al. (1995). When we use visual, 'subjective' wiggle-matching, our eyes appear to reconstruct the shape of the sequence of peat dates by connecting the data points with 'invisible lines', and compare this shape with that of the calibration curve. If we imagine such lines, the matches with a reservoir effect as shown in Fig. 1A–D become far more convincing than the matches without a reservoir effect (Fig. 1E–H). Besides this 'visual' approach, there is the 'statistical' approach where the best match is the one with the least amount of scatter (e.g., Blaauw et al., 2003). Indeed, in the studied cases, the scatter between the dates of the peat core and those of the calibration curve is less when a reservoir effect is assumed (Fig 1; Kilian et al., 1995). However, scatter of a wiggle-matched sequence of ^{14}C dates could be expected because of errors in the ^{14}C dates and/or in the growth model (Blaauw et al., 2003). All peat cores in Fig. 1 had been wiggle-matched assuming linear accumulation throughout the intervals considered, although the lithologies of several of the cores showed considerable changes, possibly indicating changes in accumulation rate. Furthermore, even when a reservoir effect is assumed, some dates still show considerable (positive and negative) scatter (Fig. 1). Moreover, the enhanced fit when assuming a reservoir effect comes at a cost, because an extra factor has to be induced and estimated (the size of the reservoir effect), and also because the origin of the supposed reservoir effect remains unknown (see below).

Because plants differentiate against ^{13}C and ^{14}C in favour of ^{12}C (fractionation), somewhat lower amounts of the heavier carbon isotopes accumulate in plants than are present in the atmosphere. In Fig. 3 the $\delta^{13}C$ values of several bog plant remains are plotted; plants growing on wetter locations clearly differentiate less against ^{13}C (higher water contents result in higher diffusion resistance; Price et al., 1997). Because of this fractionation, wet growing species are relatively more depleted in ^{14}C and thus appear relatively 'old' if their ^{14}C ages are not corrected for fractionation using their $\partial^{13}C$ values (according to Mook and Streurman (1983), a 1‰

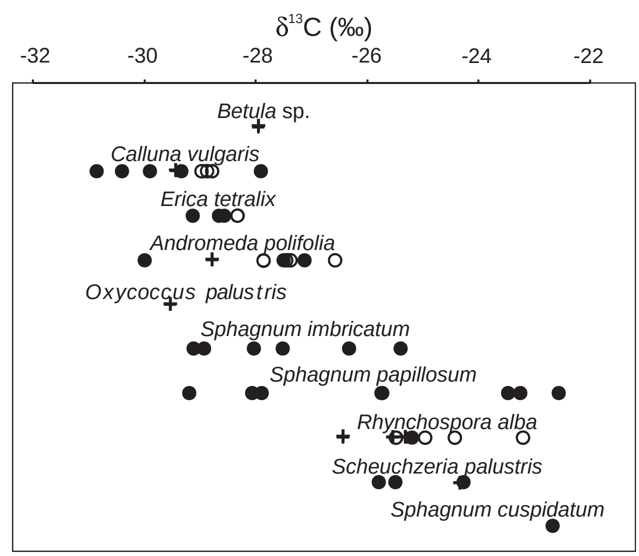

Fig. 3. Of above-ground remains from several raised bog plant species, the $\delta^{13}C$ values are plotted. Hummock (relatively dry) species such as *Calluna vulgaris* show more negative $\delta^{13}C$ values than do hollow (relatively wet) species such as *Sphagnum cuspidatum.* Species with less specific moisture requirements, such as *S. papillosum*, appear to have a wider range of $\delta^{13}C$ values. Core Eng-XV (closed circles) consisted of a hummock, while core Eng-XVI (crosses) and especially core MSB-2 K (open circles) had accumulated at wetter conditions (Blaauw, 2003; Blaauw et al., 2004a,b).

depletion of ^{13}C would make a sample 16 ^{14}C years older). In the past, ^{14}C dates were not always corrected for fractionation, possibly making some dates too old. This could be the case for core Draved Mose, where according to Aaby and Tauber (1975) the ^{14}C dates had not been corrected for fractionation. All other ^{14}C dates discussed in the present paper have been corrected for fractionation.

Different fractions of bulk peat (humin, humic acids and fulvic acids) often show distinct ^{14}C ages. In order to extract humic acids and date the humin fraction only, samples are commonly treated with acid and alkali (Mook and Streurman, 1983). All ^{14}C samples of core Eng-VII were treated with acid and alkali, while some samples of core Eng-I were either treated with acid only or with alkali only; in this case the different treatments did not result in significantly different ^{14}C ages (data not shown). The samples from Draved Mose (Aaby and Tauber, 1975) and Haslacher See (Küster, 1988) had not been subjected to humic acid extraction, and this, together with the finding that our KOH extract showed an older ^{14}C age than those of the humin fractions (Table 1), might point to humic acids causing too old ^{14}C ages. However, Dresser (1970) found that humic acid fractions of (mainly blanket mire) peat consistently yielded too *young* dates, and Nilsson et al. (2001) found that alkali hydrolysed bulk samples fractions showed *older* ^{14}C ages than did non-treated fractions. Shore et al. (1995) present even more confusing results; in their study some humin fractions dated several hundreds of ^{14}C years older than the humic acid fractions, while in other samples the opposite was found (their study was based on non-raised bog peat).

4. Conclusions

Kilian et al. (1995) postulated the existence of a reservoir effect in ^{14}C dates of bulk peat samples. However, this phenomenon could not be confirmed in the present study. Peat bulk ^{14}C dates could thus be more reliable than Kilian et al. (1995) and others (Shore et al., 1995; Nilsson et al., 2001) suggest. The evidence for reservoir effects identified by Kilian et al. (1995) was based on cores collected from different local conditions (hummocks, hollows). The core reported in the present paper consisted of a hummock (relatively dry conditions) during the investigated period. It would be interesting to repeat the present study using a core that had accumulated during lawn or hollow conditions, even more because mosses growing in hollows could contain a portion of recycled CO_2 from deeper peat layers (Price et al., 1997; Smolders et al., 2001).

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